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ASAHI DENKA KOGYO KK *JP 2002128886-A
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Catalyst composition for polymerization of propylene oxide with high controllability of very high molecular weight by use of polyetherpolyols, product being used in adhesives, surfactants, etc.
C2002-165874

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NOVELTY

Propylene oxide polymerization catalyst comprising (1) crown ether compound, (2) alkali metal alkoxide or alkali metal hydroxide and (3) polyetherpolyol of Mn (number average molecular weight) of 50-10000 and (4) trialkyl-Al compound provides PPO (polypropylene oxide) with well controlled molecular weight and used in adhesives, surfactants and urethane resins.

USE

Used in adhesives, surfactants and urethane resins.

ADVANTAGE

Product catalyst provides a manufacturing method of well controlled and high molecular weight PPO and PPO/PEO block copolymer.

EXAMPLE

Terms: t-BuOK = potassium tert-butoxide. $Al(i\text{-}(Bu)_3$ = tri-iso-butyl aluminum. Example 1: Solution of t-BuOK 1 mmol and 18-crown-6 1 mmol and $Al(i\text{-}(Bu)_3$ 3 mmol in diethylether was added with PPG (Mn = 3500) 1 mmol, removing ether at reduced pressure and heated at 100°C for 1 hour. Then at room temperature and ordinary pressure, added with 900 mmol of propyleneoxide (PO), allowing polymerization mildly and evolving some heat. 3 days later, conversion of PO reached 100%, giving PPO with Mn = 25100, Mw/Mn = 1.4. Example2: Solution of t-BuOK 1 mmol and 18-crown-6 1 mmol and $Al(i\text{-}(Bu)_3$ 5 mmol in diethylether was added with PEG (Mn = 4600) 1 mmol, removing ether at reduced pressure and heated at 100°C for 1 hour. Then at room temperature and ordinary pressure, added with 600 mmol of PO, allowing polymerization mildly and evolving some heat. 6 days later, conversion of PO reached 100%, giving a block copolymer with Mn = 17500, Mw/Mn = 1.5.

TECHNOLOGY FOCUS

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olymers - Preferred Components: Said crown ether compound is at least one of 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6 and dicyclo hexano-18-crown-6. Preferred Components: Said alkali metal alkoxide is at least one of methoxide, ethoxide, propoxide and butoxide of Cs, Rb, K, Na and Li. Preferred Components: Alkali metal hydroxide is at least one of hydroxide of Li, Na, K, Cs and Rb. Preferred Components: Said polyetherpolyol is at least one of PPG (polypropylene glycol) and PEG (polyethylene glycol) with Mn of from 50 to 10000 respectively.
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PATENT ABSTRACTS OF JAPAN

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(54) CATALYST COMPOSITION FOR POLYMERIZATION OF PROPYLENE OXIDE POLYMER AND PREPARATION METHOD OF THE POLYMER

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a polymerization catalytic composition capable of controlling the molecular weight of a propylene oxide polymer and forming the propylene oxide polymer having a high molecular weight and also to provide a preparation method of the propylene oxide polymer using the catalyst composition.
SOLUTION: The polymerization catalytic composition for a propylene oxide polymer comprises (1) a crown ether compound, (2) an alkali metal alkoxide or an alkali metal hydroxide, (3) a polyether polyol having the number average molecular weight of 50 to 10,000 and (4) a trialkylaluminum compound. The method for preparing the propylene oxide polymer using the catalyst is also provided.

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* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (1) The polyether polyol of a crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and the (3) number average molecular weight 50-10000, and the polymerization-catalyst constituent of the propylene oxide containing (4) trialkylaluminium compounds.

[Claim 2] (1) The polymerization-catalyst constituent of the propylene oxide according to claim 1 which are at least one sort of compounds chosen from the group which a crown-ether compound becomes from 18-crown -6, benzo 18-crown -6, dibenzo 18-crown -6, and dicyclohexano-18-crown-6.

[Claim 3] (2) The polymerization-catalyst constituent of the propylene oxide according to claim 1 which are at least one sort of compounds chosen from the group which an alkali-metal alkoxide becomes from caesium, a rubidium, a potassium, sodium, the methoxide of a lithium, ethoxide, propoxide, and butoxide.

[Claim 4] (2) The polymerization-catalyst constituent of the propylene oxide according to claim 1 which are at least one sort of compounds chosen from the group which an alkali-metal hydroxide becomes from a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, a cesium hydroxide, and a hydroxylation rubidium.

[Claim 5] (3) The polymerization-catalyst constituent of the propylene oxide according to claim 1 whose polyether polyol is at least one sort chosen from the group which consists of a polypropylene glycol of number average molecular weight 50-10000, and a polyethylene glycol of number average molecular weight 50-10000.

[Claim 6] (4) The polymerization-catalyst constituent of the propylene oxide according to claim 1 which are at least one sort of compounds chosen from the group which a trialkylaluminium compound becomes from triisobutylaluminum, a triethylaluminum, a trimethylaluminum, and triphenyl aluminum.

[Claim 7] (1) The poly (propylene oxide) manufacture method characterized by carrying out the polymerization of the propylene oxide under existence of the polymerization-catalyst constituent containing the polyether polyol and (4) trialkylaluminium compounds of a crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and the (3) number average molecular weight 50-10000.

[Claim 8] (3) The poly (propylene oxide) manufacture method according to claim 7 that a polyether polyol is a polypropylene glycol.

[Claim 9] (1) The manufacture method of the block copolymer of ethylene oxide and a propylene oxide characterized by carrying out the polymerization of the propylene oxide under existence of the polymerization-catalyst constituent containing the polyethylene glycol and (4) trialkylaluminium compounds of a crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and the (3) number average molecular weight 50-10000.

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* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the manufacture method of the polymerization-catalyst constituent of a propylene oxide, and a propylene-oxide polymer, and the manufacture method of the block copolymer of ethylene oxide and a propylene oxide. It is related with the polymerization-catalyst constituent and the manufacture method of manufacturing poly (propylene oxide) which has high molecular weight in more detail.
[0002]
[Description of the Prior Art] Even if it polymerization-makes the polymerization of the propylene oxide hard to carry out as compared with ethylene oxide, that the molecular weight of product polymer is comparatively low cannot carry out control of molecular weight easily in a many still higher molecular weight region, either. Then, research is advanced focusing on the initiator and the catalyst to obtain the polymer of the amount of macromolecules moreover, controlling the molecular weight of the polymer obtained.
[0003] By the method [metallic element] using aluminum or a zincky porphyrin complex, there is a report which obtained poly (propylene oxide) of a registration bundle and the amount of macromolecules about a propylene oxide until now. However, by this method, industrially, it cannot be said to be advantageous to use the porphyrin complex which it is expensive and is hard to come to hand, but a porphyrin complex is a compound with a deep color, and, moreover, it causes poly (propylene oxide) coloring used as a product.
[0004] Moreover, although poly (propylene oxide) of the amount of macromolecules is obtained also by the method using a double metal cyanide complex like hexa cyano cobalt acid zinc complex Zn3[Co(CN)6]2, removing it poses a industrial problem from poly (propylene oxide) of a product. Furthermore, it was difficult to carry out the polymerization of the propylene oxide from the ends of the block portion of high-polymer ethylene oxide conventionally about the block copolymer of ethylene oxide and a propylene oxide. Then, this invention person proposed the polymerization-catalyst constituent containing trialkylaluminium compounds, such as a crown-ether compound and an alkali-metal hydroxide, in Japanese Patent Application No. No. (JP,2000-256457,A) 061615 [11 to] that such a trouble should be improved. However, it is becoming clear that there is room of improvement in manufacturing the polymer of the amount of macromolecules practical further.
[0005]
[Problem(s) to be Solved by the Invention] The purpose of this invention can control the molecular weight of polymer, and is to offer the poly (propylene oxide) manufacture method of high molecular weight of having used the polymerization-catalyst constituent and this polymerization-catalyst constituent of the propylene oxide which can moreover make poly (propylene oxide) of high molecular weight generating. Moreover, it is in offering the manufacture method with the block of high-polymer ethylene oxide of the block copolymer of the ethylene oxide of high molecular weight, and a propylene oxide of having used this polymerization-catalyst constituent.
[0006]
[Means for Solving the Problem] As a result of inquiring wholeheartedly that the above-mentioned technical problem should be solved, when this invention persons faced carrying out the polymerization of the propylene oxide and obtaining poly (propylene oxide) and the special polymerization-catalyst constituent was used, the polymerization of a propylene oxide was made very good and, moreover, they found out that the molecular weight was high. Moreover, when this polymerization-catalyst constituent was used, it finds out that the block copolymer of the ethylene oxide of high molecular weight and a propylene oxide which the propylene-oxide block combined with the ends of a high-polymer ethylene oxide block is obtained, and came to

complete this invention.
[0007] That is, this invention offers the polyether polyol of (1) crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and the (3) number average molecular weight 50-10000, and the polymerization-catalyst constituent of the propylene oxide containing (4) trialkylaluminium compounds.
[0008] Moreover, this invention offers the polymerization-catalyst constituent of the aforementioned propylene oxide which are at least one sort of compounds chosen from the group which (1) crown-ether compound becomes from 18-crown -6, benzo 18-crown -6, dibenzo 18-crown -6, and dicyclohexano-18-crown-6.
[0009] Moreover, this invention offers the polymerization-catalyst constituent of the aforementioned propylene oxide which are at least one sort of compounds chosen from the group which (2) alkali-metal alkoxide becomes from caesium, a rubidium, a potassium, sodium, the methoxide of a lithium, ethoxide, propoxide, and butoxide.
[0010] Moreover, this invention offers the polymerization-catalyst constituent of the aforementioned propylene oxide which are at least one sort of compounds chosen from the group which an alkali-metal hydroxide becomes from a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, a cesium hydroxide, and a hydroxylation rubidium.
[0011] Moreover, this invention offers the polymerization-catalyst constituent of the aforementioned propylene oxide whose (3) polyether polyols are at least one sort of more than compounds chosen from the group which consists of a polypropylene glycol of number average molecular weight 50-10000, or a polyethylene glycol of number average molecular weight 50-10000.
[0012] Moreover, this invention offers the polymerization-catalyst constituent of the aforementioned propylene oxide which are at least one sort of compounds chosen from the group which (4) trialkylaluminium compounds become from triisobutylaluminum, a triethylaluminum, a trimethylaluminum, and triphenyl aluminum.
[0013] Moreover, this invention includes the poly (propylene oxide) manufacture method characterized by carrying out the polymerization of the propylene oxide under existence of the polymerization-catalyst constituent containing the polyether polyol and (4) trialkylaluminium compounds of (1) crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and the (3) number average molecular weight 50-10000. Here, it is desirable that a polyether polyol is a polypropylene glycol.
[0014] Moreover, this invention includes the manufacture method of the block copolymer of ethylene oxide and a propylene oxide characterized by carrying out the polymerization of the propylene oxide under existence of the polymerization-catalyst constituent containing the polyethylene glycol and (4) trialkylaluminium compounds of (1) crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and the (3) number average molecular weight 50-10000.
[0015]
[Embodiments of the Invention] In this invention, the polyether polyol of (1) crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and the (3) molecular weight 50-10,000 and the polymerization-catalyst constituent of the propylene oxide which makes (4) trialkylaluminium compounds a principal component are used on the occasion of the polymerization of a propylene oxide.
[0016] (1) It is an annular polyether and the whole ring serves as a multidentate ligand with an electron-donative oxygen atom, and a crown-ether compound will not be limited especially if it is a compound with the function to incorporate the ion of alkali metal in hole of a ring.
[0017] As these compounds, 18-crown -6, benzo 18-crown -6, benzo 15-crown -5, dibenzo 18-crown -6, dibenzo 18-crown -3, dibenzo 24-crown -8, dibenzo 30-crown -10, dicyclohexano-18-crown-6, dicyclohexano-24-crown-8, etc. can be mentioned. The alkali-metal ion which can use preferably 18-crown -6, benzo 18-crown -6, dibenzo 18-crown -6, and dicyclohexano-18-crown-6, and is incorporated especially has desirable potassium ion. Moreover, (1) crown-ether compound can also use two or more sorts together if needed.
[0018] (2) An alkali-metal alkoxide or especially an alkali-metal hydroxide does not limit the kind. For example, as an alkali-metal alkoxide, methoxides, such as caesium, a rubidium, a potassium, sodium, and a lithium, ethoxide, propoxide, butoxide, etc. can be mentioned. Potassium t-butoxide can be used especially preferably.
[0019] As an alkali-metal hydroxide, a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, a cesium hydroxide, a hydroxylation rubidium, etc. can be mentioned, for example. A potassium hydroxide can be used especially preferably. Moreover, (2) alkali-metal alkoxide or an alkali-metal hydroxide can also use two or more sorts together if needed.

[0020] (3) The polyether polyols of number average molecular weight 50-10000 are a polyethylene glycol and a polypropylene glycol. especially a desirable thing -- the number average molecular weight 50-5000 from the plain-gauze fibers for plastering of acquisition -- it is the thing of 50-3000 preferably Moreover, the polyether polyol of the (3) number average molecular weight 50-10000 can also use two or more sorts together if needed. Moreover, when a polyethylene glycol is used, the block copolymer of an ethylene oxide and a propylene oxide with the high-polymer ethylene oxide block is obtained, the portion of ethylene oxide of this block copolymer is hydrophilic, and the portion of a propylene oxide is hydrophobic and useful as a surfactant. According to this invention, by making a catalyst constituent contain the polyether polyol of the (3) number average molecular weight 50-10000, a reaction advances by making the hydroxyl of the end of a polyether polyol into a start point, and it is considered that it can manufacture the polymer of the amount of macromolecules compared with the case where this polyether polyol is not used.
[0021] (4) It has branching respectively independently, or the substituents which the trialkylaluminium compound acted as a Lewis acid and were combined with the aluminum atom can be the shape of a chain without branching, and an annular thing, and are the alkyl group or aryl group of carbon numbers 1-20. moreover, ** which was crowded in three dimensions about the coordination position of the circumference of the aluminum atom with which the substituent combined with the aluminum atom serves as a Lewis acid and which gives the limited space -- a high substituent is desirable
[0022] As a trialkylaluminium compound, although triisobutylaluminum, a triethylaluminum, a trimethylaluminum, triphenyl aluminum, etc. are mentioned, triisobutylaluminum can be used especially preferably, for example. Moreover, two or more sorts of (4) trialkylaluminium compounds can also be used together if needed.
[0023] In a solvent, after that, (3) polyether polyol can be added to the solution containing (1) crown-ether compound, (4) trialkylaluminium compounds and (2) alkali-metal alkoxide, or an alkali-metal hydroxide, the catalyst of this invention distills off, and a solvent is made to be able to heat and it can obtain it. Carry out stirring mixture, (1) crown-ether compound, (4) trialkylaluminium compounds, and (2) alkali-metal alkoxide or an alkali-metal hydroxide is made to react in a suitable solvent as the poly (propylene oxide) manufacture method using the polymerization-catalyst constituent of this invention, or the manufacture method of the block copolymer of ethylene oxide and a propylene oxide, and reduced pressure distilling off of the solvent is carried out after that. Subsequently, (3) polyether polyol is added further and the mixture is made to react at the temperature around bottom 100 degrees C of reduced pressure. And the polymerization of the propylene oxide of an initial complement is added and carried out.
[0024] (1) As for a crown-ether compound, it is desirable to use one mols or more to one mol of alkali-metal ion of (2) alkali-metal alkoxide or the alkali-metal hydroxide origin. A reaction rate falls in less than one mol. The range of (1) crown-ether compound is 1-2 mols to one mol of alkali-metal ion preferably.
[0025] (2) Although the amount of an alkali-metal alkoxide or the alkali-metal hydroxide used can also be chosen arbitrarily, it is a mole ratio to a propylene oxide preferably, and is 0.05 - 1% more preferably 0.05 to 10%.
[0026] (3) Although the amount of a polyether polyol can be chosen arbitrarily, the ranges of the mole ratio of the hydroxyl group in a polyether polyol, and (2) alkali-metal alkoxide or the alkali-metal ion of the alkali-metal hydroxide origin are 1:1-5:1 preferably. The ratio is 1:1 more preferably.
[0027] (4) Although the amount of a trialkylaluminium compound can also be chosen arbitrarily, the mole ratio of a trialkylaluminium compound and the hydroxyl group in a polyether polyol is more than one (1:1) preferably. The ratio is 1:1-3:1 more preferably. In more than three (3:1), the polymerization of a propylene oxide may happen violently and it may be dangerous.
[0028] Although there is a place which still is not clear about the role of the polymerization-catalyst constituent of this invention, a crown-ether compound carries out the inclusion of the alkali-metal ion produced from an alkali-metal alkoxide or an alkali-metal hydroxide, the propylene oxide of a monomer configurates in the aluminum atom in the alkylaluminum compound which acts as a Lewis acid by one side, and the anion kind produced from the alkali-metal alkoxide or the alkali-metal hydroxide is considered that a polymerization is started smoothly by carrying out a nucleophilic attack to a coordination propylene oxide.
[0029] The molecular weight of the block copolymer of poly (propylene oxide) or ethylene oxide obtained, and a propylene oxide is controllable by adjusting the alkali-metal alkoxide or alkali-metal hydroxide used as the source of the anion kind of a nucleophile, and the mole ratio of a propylene oxide with this invention.

[0030] Its ether is desirable although the solvents to be used are ether, ketones, ester, aliphatic hydrocarbon, aromatic hydrocarbons, a halogen system solvent, etc.
[0031] Especially if reaction temperature is general temperature, it will not be limited, but its room temperature is desirable. The block copolymer of poly (propylene oxide) or ethylene oxide obtained by this invention, and a propylene oxide is applicable to various uses. For example, it can use as adhesives, a urethane-resin raw material, a surfactant raw material, etc.
[0032]
[Example] Hereafter, although an example explains this invention further, this invention is not limited to these examples. In addition, the reaction was performed under inert gas and non-water atmosphere. A reactant is sampled, it dissolves in the methanol and tetrahydrofuran (THF) of a proper quantity, and the molecular weight and molecular weight distributions Mw (weight average molecular weight)/Mn (number average molecular weight) of a product evaporated it, and were remelted to THF, measured GPC (for THF) after filtration with the Teflon (registered trademark) filter, and calculated it by polystyrene conversion. Moreover, the yield of a reaction also sampled the reactant and computed it from the result of 1 H-NMR.
[0033] After Mn added 1mmol for the polypropylene glycol (PPG3500) of 3500 to the potassium tertiary butoxide (t-BuOK) of example 11mmol, the 18-crown -6 of 1mmol, and the solution of diethylether containing the triisobutylaluminum (aluminum3 (i-Bu)) of 3mmol, reduced pressure distilling off was carried out and the ether was heated at 100 degrees C under reduced pressure as it was for 1 hour. And it returned to the ordinary-pressure room temperature, and the propylene oxide was added 900 mmols. The polymerization advanced generating heat quietly. Three days after, the invert ratio of a propylene oxide reached to 100%, and the results of obtained poly (propylene oxide) GPC were Mn=25100 and Mw/Mn=1.4.
[0034] The 18-crown -6 of t-BuOK of example 21mmol, and 1mmol, aluminum3 of 5mmol (i-Bu) After Mn added 1mmol for the polyethylene glycol (PEG4600) of 4600 to the solution of included diethylether, reduced pressure distilling off was carried out and the ether was heated at 100 degrees C under reduced pressure as it was for 1 hour. And it returned to the ordinary-pressure room temperature, and the propylene oxide was added 600 mmols. The polymerization advanced generating heat quietly. Six days after, the invert ratio of a propylene oxide reached to 100%, and the results of GPC to the block copolymer of the obtained ethylene oxide and a propylene oxide were Mn=17500 and Mw/Mn=1.5.
[0035]
[Effect of the Invention] According to this invention, the molecular weight of polymer can be controlled and the manufacture method using the polymerization-catalyst constituent and this polymerization-catalyst constituent of the propylene oxide which can moreover compound the block copolymer of the poly (propylene oxide), the ethylene oxide, and the propylene oxide of high molecular weight is offered. Especially this invention is characterized by obtaining the polymer of the amount of macromolecules compared with the case where this is not used by using (3) polyether polyol.

[Translation done.]